

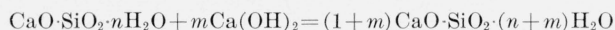
# A Thermochemical Study of the Reaction of Calcium Hydroxide, Silica Gel, and Water

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The heat of reaction of calcium hydroxide, silica gel, and water was measured by a heat-of-solution method. The reaction was carried out at 25° C in pastes having a water solid ratio of about 1.0. The heat of reaction,  $-\Delta H$  at 25° C, for the reaction



was found to be about 10.3 kilocalories. The heat of the reaction



is about 1.6 kilocalories per mole of added  $\text{Ca(OH)}_2$ . About half of the total measured heat of reaction represents the heat of wetting of the reaction products. Differential thermal analyses and drying experiments indicated that  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  was formed in some of the pastes.

## 1. Introduction

The reactions of lime with silica and water are of fundamental importance in the study of the hydration of portland cement, and are of particular interest in the study of the effect of pozzolans. The energy changes occurring dictate the direction and extent to which the reactions may proceed, and a knowledge of these changes will aid in elucidating the mechanism of the process.

Measurements of the heat of reaction of lime with silica and water fall into three general classes: (1) Determination of the heat of hydration of portland cement; (2) determination of the heat of hydration of the individual compounds occurring in cement; and (3) measurement of the heat of reaction between calcium hydroxide solutions and silica gel. Woods, Steinour, and Starke [1]<sup>1</sup> developed the heat-of-solution method of determining the heat of hydration of portland cement, which has evolved into an acceptance test [2,3] for use when it is important to limit the heat evolved during the setting of concrete. Others [4,5,6] have measured the heat of hydration by direct methods, which are, however, limited to relatively short periods. The results of measurements falling in the first group are useful for control and have been extended to determining the contribution of the individual constituents of the cement to the heat of hydration. The direct measurements have been useful in explaining the important reactions that occur in the early stages of the setting of concrete.

The measurements of the heat of hydration of the individual compounds of portland cement have almost without exception been made by the heat-of-solution method. Lerch and Bogue [7], Brunauer, Hayes, and Hass [8], Brisi [9], Thorvaldson, Brown, and Peaker [10], Cirilli [11], and others have determined the heat of reaction of individual compounds with water. Many of these measurements were made with pastes of hydraulic material and water, approximating the proportions and consistency used in placing or testing portland cement. The heats of

reaction obtained have been used to aid in the identification of the reaction products [8].

The third class of measurements, also made by the heat-of-solution method, have been made on the reaction products obtained [11, 12, 13] by the reaction between calcium hydroxide solution and silica gel performed in such a manner that a large quantity of solution came into contact with a small quantity of silica gel. These measurements also have been used to aid in identifying the reaction products obtained.

The present paper is the report of the results of heat-of-solution measurements made at intervals over an extended period on pastes of calcium hydroxide, water, and silica gel. The constituents were finely divided and in intimate contact with each other and with the small amount of water, so that local depletion of the calcium hydroxide in solution might be avoided. These measurements should agree with those made in class three above, and together with those of both class two and class three, should provide data for calculating the heats of formation of the reaction products.

## 2. Apparatus, Materials, and Procedure

### 2.1. Calorimetry

The heat-of-solution method of measuring the heat of a reaction was used in this work. The procedure consists in measuring the heats of solution of the reactants and the products of the reaction under investigation. A solvent in which all the materials will dissolve should be chosen, or proper corrections made for the heat effects of any insoluble substances. The final solution at the end of the heat-of-solution experiment made with the products must be identical in molar concentration and quantity with the final solution obtained at the end of the heat-of-solution experiment made with the reactants, or the heat effects of the reactions necessary to bring the two final solutions to identity must be obtained and used in the computations. Under these conditions, the heat of the reaction is the difference between the

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

sums of the heats of solution of the products and the sums of the heats of solution of equivalent amounts of the reactants in the same solvent.

In the present work, 1- to 2-g samples of hydrated paste were dissolved in a mixture of nitric and hydrofluoric acids. A total weight of 600.0 g of acid was used, of which 12.6 g (11.0 ml) was 48 percent HF, the remainder being  $\text{HNO}_3, 26.03\text{H}_2\text{O}$  (2.000 N at 25° C) [14]. The composition of the calorimeter acid charge was therefore 0.302HF, 1.10  $\text{HNO}_3, 29.11\text{H}_2\text{O}$ . Because some of the earlier work [9, 11, 12, 13] had been done with hydrochloric acid, some determinations were made using 600.0 g of  $\text{HCl}, 26.61\text{H}_2\text{O}$  (2.000 N at 25° C) [14]. The heats of solution at 25° C were determined in an isothermal-jacket, platinum-lined calorimeter which has been described previously [15]. At the end of determinations in which HCl was used, the calorimeter acid was filtered and the undissolved silica recovered and weighed.

In determinations of the heat of solution using the nitric-hydrofluoric acid mixture, the quantity of sample dissolved was kept small enough to avoid the precipitation of  $\text{CaF}_2$ . In this manner the necessity of correcting for the heat effect of the precipitation was avoided. If precipitation occurs, about 9.1 kcal will be evolved for each mole of  $\text{CaF}_2$  so formed [16], and the heat of solution obtained will be too high. The data of Brunauer, Kantro, and Weise [17] showed a heat effect of about 60 cal/g of CaO (3.4 kcal/mole) in excess of the normal value of the heat of solution of the CaO when the sample size was increased above about 0.37 g (in 420 g of mixed acids), where precipitation of  $\text{CaF}_2$  was observed to begin. With calcium hydroxide in the present work with a larger calorimeter, the corresponding increase was about 20 cal/g of  $\text{Ca}(\text{OH})_2$  (1.5 kcal/mole) when the sample size was increased above about 1 g. It is evident that in both investigations only partial precipitation of  $\text{CaF}_2$  occurred, as the full increase corresponding to 9.1 kcal/mole was not obtained. It has been observed that when the CaO is combined in a silicate much larger samples can be dissolved without precipitating  $\text{CaF}_2$ . With portland cement, for example, it is possible to dissolve completely 3-g samples in 425 g of mixed nitric-hydrofluoric acid [2] without precipitation of calcium fluoride, although there is approximately 1.5 g of CaO in the sample.

## 2.2. Differential Thermal Analysis

Differential-thermal-analysis curves were obtained with an apparatus that has been described previously [18]. The curves were recorded automatically, and the heating rate, controlled by a motor-driven variable transformer rotated at constant speed, was about 12.5 deg C/min.

## 2.3. Preparation of the Pastes

All materials were chemicals of analytical reagent quality. Single lots of calcium hydroxide and silicic acid were used in preparing all the pastes, in order to reduce possible variations in the results

caused by differences in surface or other properties of the starting material.

The calcium hydroxide and the silica gel were heated over night at 1,200° C to obtain the losses on ignition. The residues were taken to be CaO and  $\text{SiO}_2$ , respectively. Seventy-gram mixtures of the unignited materials were prepared, weighing the components to the nearest 0.01 g. The weight of each material to be used was calculated from its ignition residue and the desired C/S ratio.<sup>2</sup> Fifteen mixtures were prepared over the range of molar C/S ratios from 0.3 to 3.3 in such a way as to bracket and to include the simple ratios 0.5, 1.0, 1.5, 2.0, and 3.0. The weighed materials were tumbled for 2 hr in bottles with a few wooden balls to insure uniformity of composition.

The individual mixtures were mixed with distilled water and stored in wax-sealed glass vials in the manner described in Federal Specification SS-C-158c [2]. A water-solids ratio of about 1.0 was used in order to obtain pastes with sufficient fluidity to fill the vials easily.

## 2.4. Testing the Hardened Pastes

One vial of each mixture was opened for testing at the ages of 1, 7, and 28 days, 16 weeks, and 1 and 2½ years. The samples were dried under vacuum for about 1 hr until enough water had been removed from the damp samples so that they could be crushed and passed through a No. 28 sieve without caking. The total residual water content of samples thus treated was about 50 percent. Crushing and sieving were done as expeditiously as possible to reduce reaction with  $\text{CO}_2$  in the atmosphere. The samples were then placed in small rubber-stoppered Erlenmeyer flasks for ease in shaking. Portions were removed for heat-of-solution and loss-on-ignition measurements,  $\text{CO}_2$  determinations, and chemical analysis. Only the first two measurements were made on every sample tested. The individual weighed portions of each paste were taken consecutively as quickly as possible, so that one loss-on-ignition value could be applied to all the samples of a single paste. The analytical procedures were started at once, and the heat-of-solution measurements were made thereafter, usually within 2 hr. The samples for the latter test were kept in weighing bottles until used, and no significant change of weight occurred in this period.

## 3. Results and Discussion

### 3.1. Heats of Solution of Calcium Hydroxide and Silica Gel

Twelve determinations of the heat of solution of  $\text{Ca}(\text{OH})_2$  in the  $\text{HNO}_3$ -HF mixture were made using samples of 0.8 to 1.0 g. No precipitation of  $\text{CaF}_2$  was observed. Although the scatter was rather larger than desired, there appeared to be no correla-

<sup>2</sup> The usual notation of C=CaO, S= $\text{SiO}_2$ , and H= $\text{H}_2\text{O}$  will be used. The molar ratio CaO/ $\text{SiO}_2$ , for example, will be written as C/S.

tion with sample size over this short range. The individual values of the heats of solution were calculated to a molar basis on the assumption that the ignition residue was CaO. The average value,  $31.70 \pm 0.10$  kcal/mole,<sup>3</sup> was somewhat higher than that given by Brunauer, Hayes, and Hass [8] but agreed with the value 31.7 calculated from data available in NBS Circular 500 [16]. The experimental value 31.70 kcal/mole was used for the heat of solution of calcium hydroxide in calculating the heat of reaction of calcium hydroxide and silica gel.

Eight determinations of the heat of solution of the silica gel were made using samples of 1.0 to 2.0 g. The average value  $34.78 \pm 0.13$  kcal/mole was obtained and used in calculations. Roth and Chall [21] obtained  $34.49 \pm 0.02$  kcal/mole at 50° C for silica gel containing about 66.7 percent of water. According to Mulert [22], the heat of solution of silica gel containing 10 percent of water is about 0.24 kcal/mole higher than that of gels containing large amounts of water. In calculations comparing heats of reaction obtained in this investigation with the results of others, correction has been made for this 0.24 kcal.

After removal of the weighed portions for the above mentioned tests, the remainder of the crushed sample was returned to the evacuation chamber until the following day when differential thermal analyses were made and, in some cases, X-ray patterns were obtained. At 1 and 2½ years the parts of the samples remaining after the usual first-day tests were evacuated through a dry-ice trap, according to the procedure of Copeland and Hayes [19], and the heat-of-solution measurements were repeated.

In general, standard analytical procedures were used [2]. The sample for the determination of loss on ignition was dried for 2 hr at 110° C, placed in a cold furnace, and heated to 1,200° C over night. In some of the tests when the standard analysis was not made, the residue from the loss-on-ignition test was fumed twice with HF and heated to 850° C, and the residue weighed as CaF<sub>2</sub> [20]. From the data thus obtained, the C/S ratio of the sample was calculated.

Some additional experiments were made to determine the effect of sample size on the heats of solution of calcium hydroxide and silica gel, and also to determine the effects of either material on the heat of solution of the other. It was found that, within the precision of the present work, neither predissolved Ca(OH)<sub>2</sub> nor predissolved silica gel had any significant effect on the heat of solution of the other. Variation of the size of the sample between 0.5 and 1.5 g also had no significant effect on the heat of solution of either substance. These observations were true only if calcium fluoride was not precipitated. With larger samples, if the silica gel was dissolved before the calcium hydroxide was added to the solution, no precipitation of CaF<sub>2</sub> occurred, and the normal value was obtained for the heat of solution of calcium hydroxide, even up to sample weights

of 1.5 g. However, if the calcium hydroxide was added first, a high value for its heat of solution was obtained, although seemingly insignificant amounts of precipitated CaF<sub>2</sub> were visible. If the silica gel was then added to the same solution in the calorimeter, a low value was obtained for its heat of solution, and the calcium fluoride redissolved. In one experiment the sum of the high value obtained for the heat of solution of calcium hydroxide and the low value obtained for silica gel was equal, within 1.2 cal/g, to the sum of the normal value of the heat of solution of silica gel and the value obtained for the heat of solution of calcium hydroxide, when the presence of predissolved silica gel prevented the precipitation of calcium fluoride.

The heat of solution of the calcium hydroxide in HCl, 26.61H<sub>2</sub>O (2.000 *N* at 25° C) was determined for use in calculations to be made using the heat of decomposition of the calcium hydroxide-silica gel pastes in that acid. The heat effect of adding the silica gel was also determined. The values obtained were 31.26 and 1.01 kcal/mole for the calcium hydroxide and silica gel, respectively. Tests showed that the presence of either substance previously added to the calorimeter solution did not alter significantly the heat effect obtained for the other material.

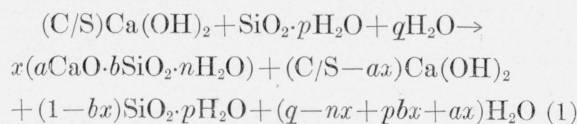
### 3.2. Heats of Solution of the Pastes

The analyses and heats of solution of the pastes are given in table 1. The heats of solution were calculated to kilocalories per mole of silica in the paste. For this purpose, the percentage of silica in the paste, *s*, was calculated from the original molar C/S ratio and the percentage residue on ignition, *R*, by the equation  $s = 1.071R / (C/S + 1.071)$ , in which 1.071 is the ratio of the molecular weights of SiO<sub>2</sub> and CaO, 60.06 and 56.08, respectively.

The C/S ratios calculated from the analyses in table 1 were usually somewhat less than the proportions weighed in making the pastes. However, these calculated ratios are affected by any analytical errors and do not allow for MgO, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, or other nonvolatile impurities in the original materials. Because the proportions of the original mixes and the molar heats of solution of the calcium hydroxide and silica gel were calculated on the basis of the ignited weights of the starting materials, the original C/S ratios were used in all computations.

### 3.3. Heats of Reaction

Based on 1 mole of silica, the equation representing the formation of a hydrated calcium silicate by the reaction of calcium hydroxide and silica gel in a paste may be written



The heat of the reaction to form the hydrated calcium silicate may be found from the difference in

<sup>3</sup> The standard deviation of the average is given here and elsewhere in this paper. Heats unless otherwise indicated refer to  $-\Delta H$  at 25° C.



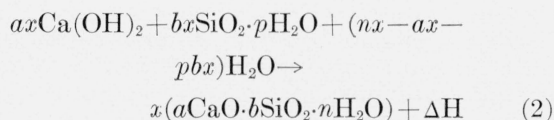
TABLE 1. Analyses and heats of solution of calcium hydroxide—silica gel pastes

Molar ratio CaO/SiO <sub>2</sub>	Age	Analytical results					Heat of solution -ΔH at 25° C		Fraction of sample insoluble in HCl	Molar ratio CaO/SiO <sub>2</sub>	Age	Analytical results					Heat of solution -ΔH at 25° C		Fraction of sample insoluble in HCl				
		CaO	SiO <sub>2</sub>	CO <sub>2</sub>	Loss on ignition	Molar ratio CaO/SiO <sub>2</sub> observed	HCl, 26.61 H <sub>2</sub> O	0.274 HF, HNO <sub>3</sub> , 26.36 H <sub>2</sub> O				CaO	SiO <sub>2</sub>	CO <sub>2</sub>	Loss on ignition	Molar ratio CaO/SiO <sub>2</sub> observed	HCl, 26.61 H <sub>2</sub> O	0.274 HF, HNO <sub>3</sub> , 26.36 H <sub>2</sub> O					
																				1	2	3	4
0.300	Days 1 7 28 28 112 365 365P 837 837P	%	%	%	%	cal/g	cal/g	%	1.600	Days 1 7 28 28 112 365 365P 917 917P	%	%	%	%	cal/g	cal/g	%						
																		50.51	259.2	60.57	50.41	261.3	3.61
																		50.47	256.9	275.7	51.46	245.0	---
																		15.57	57.6	38.56	53.92	233.0	---
																		47.31	275.7	42.00	51.64	242.8	4.75
																		49.26	34.23	38.56	40.30	232.3	3.90
																		45.24	36.08	286.9	40.30	247.4	---
																		9.48	303	514.9	12.42	232.3	2.43
																		51.03	293	256.9	52.98	241.2	---
																		10.67	---	503.7	13.06	466.0	---
																		51.46	---	251.7	48.60	271.2	---
																		50.55	---	254.9	54.47	239.7	---
51.67	---	250.5	24.33	222.1	9.59																		
50.14	390	257.8	56.73	222.1	---																		
48.24	414	266.8	50.65	250.2	3.08																		
9.72	414	510.0	50.29	248.1	1.96																		
47.79	396	269.7	2.05	467.1	---																		
11.85	---	490.1	14.55	457.9	---																		
51.76	---	245.5	51.73	255.7	---																		
53.41	---	233.9	52.37	246.4	---																		
21.03	---	92.7	52.47	244.0	---																		
53.28	---	237.8	51.30	246.2	2.65																		
49.12	498	258.7	47.06	267.0	---																		
53.96	506	234.5	15.36	461.3	2.66																		
10.51	507	499.6	2.09	227.3	2.34																		
59.79	501	205.7	54.82	451.7	---																		
11.76	---	486.6	16.30	---	---																		
52.45	---	244.0	48.02	275.1	---																		
51.22	---	249.6	53.80	240.7	---																		
51.50	---	242.8	52.55	245.0	---																		
47.82	685	260.1	49.47	259.7	2.60																		
45.66	704	266.4	42.78	290.6	1.85																		
9.75	701	499.4	2.05	457.6	---																		
50.83	690	245.0	1.31	246.8	1.55																		
10.68	---	489.5	17.42	449.8	---																		
52.55	---	246.6	51.42	262.3	---																		
53.50	---	228.5	51.33	252.9	---																		
23.56	138.5	---	51.25	251.1	---																		
53.26	---	230.6	50.48	255.4	2.15																		
49.35	880	248.1	49.74	255.2	1.39																		
49.20	904	246.5	49.74	443.6	---																		
8.83	889	494.0	17.66	443.6	---																		
43.62	877	276.1	49.96	257.5	0.86																		
10.24	---	485.1	17.86	439.8	---																		
52.42	---	246.8	48.81	273.9	---																		
53.31	---	230.7	48.57	267.9	---																		
53.93	---	229.1	53.50	242.2	---																		
49.89	969	245.1	50.45	256.2	2.54																		
45.47	982	267.3	33.37	340.2	2.39																		
8.93	985	495.9	17.75	446.1	---																		
50.81	972	105.7	44.36	285.7	1.76																		
10.74	---	475.1	17.63	446.9	---																		
50.30	---	257.5	47.94	279.8	---																		
51.07	---	248.5	50.11	260.5	---																		
49.45	---	248.3	23.76	260.5	6.09																		
46.45	1.094	261.6	51.47	253.4	---																		
43.82	1.120	275.1	48.07	268.8	2.53																		
9.59	1.105	488.6	39.84	310.2	2.33																		
49.28	1.105	247.9	60.42	452.7	---																		
11.25	---	480.1	1.37	462.2	0.97																		
52.04	---	252.2	47.94	279.8	---																		
51.16	---	248.8	50.11	260.5	---																		
49.60	---	252.5	23.76	260.5	6.09																		
50.99	1.464	243.9	51.47	253.4	---																		
42.48	1.498	285.0	48.07	268.8	2.53																		
11.54	1.475	480.3	39.84	310.2	2.33																		
50.90	1.473	242.6	60.42	452.7	---																		
13.00	---	273.8	1.37	462.2	0.97																		
44.46	---	466.8	18.37	442.4	---																		
12.84	---	---	---	---	---																		

<sup>1</sup> "P" indicates that sample was kept at water vapor pressure of about ½ micron (ice at dry ice temperature) until loss fell below 0.5 mg/day.  
<sup>2</sup> Figures in parentheses were obtained by fuming the ignition-loss sample with HF and weighing the CaF<sub>2</sub> formed, as described in the text.



the sums of the heats of solution of the products and the reactants in the usual manner. If heats of dilution are neglected, the uncombined calcium hydroxide, silica gel, and water will contribute nothing to this difference, because their molar heats of solution will be the same after the reaction as before. Equation (1) can then be rewritten



where  $\Delta H$  is the observed difference between the heat of solution of the paste containing the hydrated calcium silicate and the sum of the heats of solution of the reactants from which the paste was formed. If  $\Delta H$  is calculated per mole of silica in the whole paste, its value increases with the amount of silica entering the reaction (i. e.,  $bx$ ) until a final constant value is reached when all of the silica has been combined ( $bx=1$ ). This calculation does not depend on a knowledge of the composition of the hydrated calcium silicates formed. If the final values of  $\Delta H$  are plotted against the C/S ratios of a series of pastes, the curve will consist of a series of straight lines intersecting at the compositions of the hydrated calcium silicates formed. The slope of each line will be proportional to the heat of the reaction involved.

In the foregoing discussion a number of corrections have been neglected. These are: The heat effect of dissolving silica gel and calcium hydroxide separately rather than simultaneously, the effect of sample size on the value obtained for the heat of solution (excluding the effect of precipitated  $\text{CaF}_2$ ), and the heat effect of diluting the calorimeter acid with the

water formed in the hydration reaction or present in the paste. Experiments have already been described that showed the first two of these effects to be negligible in the present work. The heat of solution of the water contained in the paste is approximately equal to the partial molar heat content of water in  $\text{HNO}_3$ ,  $26.03\text{H}_2\text{O}$  and in  $\text{HF}$ ,  $100\text{H}_2\text{O}$ ,  $0.002$  and  $0.0004$  kcal/mole of  $\text{H}_2\text{O}$ , respectively [16]. These quantities are also negligible.

The heat-of-reaction technique was used by Cirilli [12] to determine the composition of the hydrated calcium silicate produced by the reaction between calcium hydroxide solution and silica gel. He determined the heat of decomposition of the reaction product in hydrochloric acid in calories per gram of  $\text{CaO}$ . The heat of solution calculated from these measurements remained constant up to C/S=1 and then increased with further increase in C/S. It was hoped that the procedure used in the present investigation would, by reason of the longer times of reaction and larger C/S ratios involved, give on the curve of  $\Delta H$  versus C/S ratio a more definite change of slope indicating the formation and composition of a compound containing more  $\text{CaO}$  than monocalcium silicate hydrate, such as the  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$  reported by Cirilli and others. Unfortunately this hope was not realized.

In figure 1 are shown the heats of reaction of  $\text{Ca}(\text{OH})_2$ , silica gel, and water (reaction 2) for each of the pastes of table 1, plotted as a function of the time. The major portion of the heat of reaction was released in 1 to 7 days. At C/S ratios larger than 0.5, the reaction proceeded further slowly. This behavior suggests that at any C/S ratio the monocalcium silicate hydrate reported by Cirilli was formed promptly, and that a more basic product was formed subsequently in pastes with C/S ratios

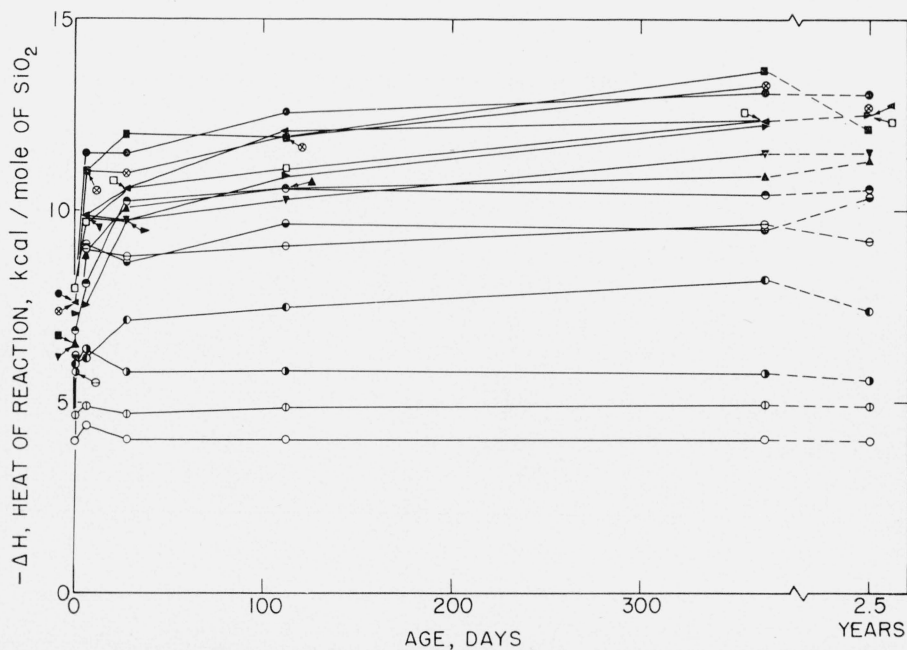


FIGURE 1.—Heat of reaction of calcium hydroxide and silica gel as a function of time of contact.

C/S	C/S	C/S
○ 0.3	● 1.0	◄ 2.3
○ 0.4	● 1.2	□ 2.5
○ 0.5	▲ 1.5	■ 2.9
● 0.7	▼ 1.6	⊗ 3.0
○ 0.9	▶ 2.0	● 3.3

larger than 1. In figure 2 are shown the heats of reaction of the pastes at 1 year plotted against the C/S ratio. The two straight lines A and B shown in the figure, represent the least-squares equations calculated from the present data for C/S ratios, for A, of 0.3 to 1.0 inclusive, and, for B, of 1.0 to 3.33 inclusive. The average value of the intersections of these two lines with C/S=1 is 10.3 kcal/mole of silica. This value is taken as the heat of reaction of calcium hydroxide and silica gel to form the monocalcium silicate hydrate. The corresponding value calculated from Cirilli's data [11,12,13] is 10.96 kcal/mole. The slope of the line between C/S=1 and C/S=3.33 is 1.58. The value of 1.6 kcal/mole of added  $\text{Ca}(\text{OH})_2$  is therefore taken as the heat of reaction of calcium hydroxide and 1 mole of monocalcium silicate at 1 year to form material of C/S ratios higher than one. This heat of reaction is so small that it easily might be heat of adsorption of calcium hydroxide on the monocalcium silicate hydrate. The precision of the data is not adequate to show definitely a change of slope indicating a change in the way the lime is combined, such as that reported by Cirilli at C/S=1.5.

The data taken at 2½ years are similar to the 1 year results. The heat of reaction and the slope of the line B were found to be 10.5 and 1.06 kcal/mole, respectively. The slightly increased amounts of  $\text{CO}_2$  found in the samples at the later age may in part account for the differences in the heat effects. No correction has been made for the small  $\text{CO}_2$  content of any of the samples. It is more likely, however, that surface or other changes in the pastes are responsible for the differences.

Brunauer, Hayes, and Hass [8] determined the heat of hydration of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  to be 22.0 and 4.1 kcal/mole, respectively. From their results the heats of reaction of  $\text{Ca}(\text{OH})_2$ , water, and silica gel

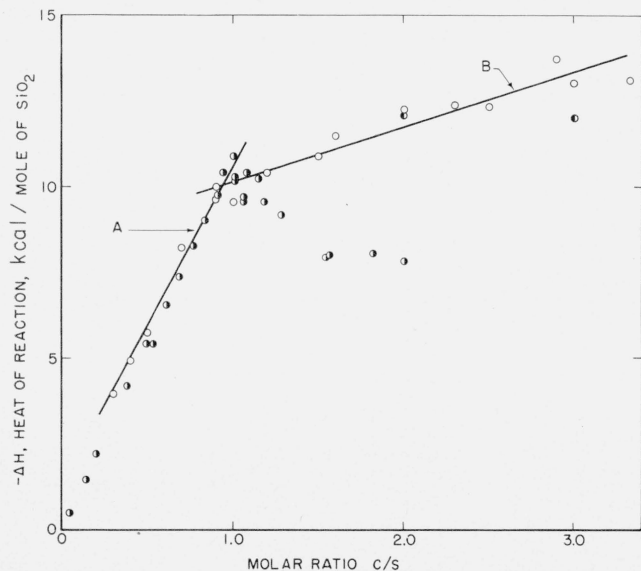


FIGURE 2.—Heat of reaction of calcium hydroxide and silica gel at 1 year.

○, Newman; ●, Brunauer, Hayes, and Hass [8]; ◐, Cirilli [11, 12, 13].

to form the hydrated calcium silicates produced by the hydration of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  have been calculated to be 11.96 and 12.13 kcal/mole, respectively. These values are plotted in figure 2. Considering the uncertainties involved, the agreement is good.

The heats of reaction calculated from Cirilli's data are also plotted in figure 2. The agreement is excellent until the C/S ratio becomes larger than 1.0. Cirilli's results are based on the assumption that the silica gel contributed nothing to the heat of solution in HCl, being precipitated at the end of the heat-of-solution experiment in its original form. In the present work this assumption could not be made, because the heats of reaction as measured with nitric-hydrofluoric acid mixtures were not the same as those determined using hydrochloric acid. A considerable amount of the silica in the paste remained dissolved in the HCl at the end of each determination, and its heat of solution was included in the measured value. In figure 3 is shown the fraction of the silica dissolved in the HCl, plotted as a function of the C/S ratio of the paste. If the soluble silica were taken as an indication of the reaction between calcium hydroxide, silica gel, and water, as was done by Shaw and MacIntire [23], it would appear that the reaction was not ended, even after the lapse of 2½ years and in the presence of excess  $\text{Ca}(\text{OH})_2$ . The measurement of the fraction of soluble silica does seem to represent some property of the paste, as it generally increases with increased age of the paste, and it would appear reasonable to correct the measured heat of reaction accordingly. However, if a correction is made, using the silica insoluble in HCl to represent unreacted silica, large (at low C/S) and inconsistent values are obtained for the heat of reaction. The values shown in figures 1 and 2, therefore, have not been corrected.

Thermochemical calculations show that the difference in the heats of reaction obtained in the two solvents may be attributed to the difference in the heat content of the silica gel in its original state, and

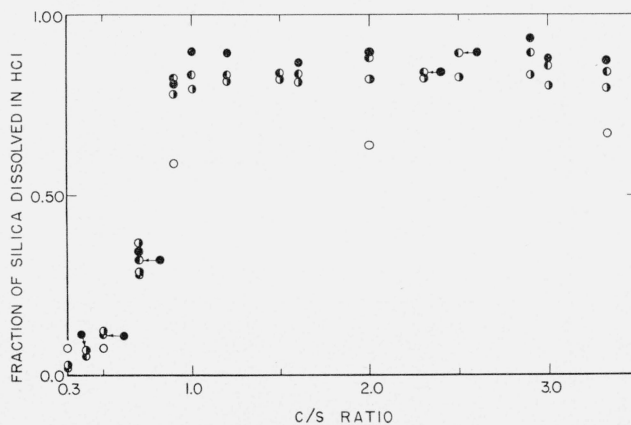


FIGURE 3.—Fraction of silica dissolved in HCl in the calorimeter.

○, 28-day; ◐, 16-week; ●, 1-year; ●, 2½-year.

as a component of the hydrochloric acid solutions resulting when the hydrated pastes were dissolved. The differences, after dividing by the fractions of the silica dissolved in the hydrochloric acid solutions, were scattered about an average value (excluding those determined at C/S ratios of less than 0.7) of  $\Delta H = -4.8 \pm 0.25$  kcal/mole of dissolved silica. This value may be considered as a measure of the heat of gelation of silica gel from the low-molecular-weight form occurring in hydrochloric acid solution. Tourky [24] has given  $\Delta H = -8.9$  kcal/mole as the heat of gelation from alkaline solution, and Greenberg [25] has estimated a value of  $-2.7$  kcal/mole for the heat of polymerization of silica gel.

### 3.4. Heat of Adsorption of Water

It has been concluded [8] that under the conditions of drying used in this work all of the water adsorbed on the hydrated calcium silicate in the paste would be removed. The difference in the heats of solution of the pastes before and after drying should, therefore, be equal to the heat of adsorption of the water. These heats of adsorption are shown in figure 4 as a function of the C/S ratio. The values found both at 1 year and 2½ years are given; the latter are generally the smaller. The heats of adsorption of water on the reactants were calculated from similar heats of solution determined before and after drying the calcium hydroxide and silica gel. The line representing the reactants is shown in figure 4, calculated from the equation  $H_{\text{SiO}_2} + (C/S)H_{\text{CaO}} = H_{\text{reactants}}$ , where  $H_{\text{SiO}_2}$  is the heat of adsorption of water on the dried silica gel (of composition  $\text{SiO}_2 \cdot 0.21\text{H}_2\text{O}$ ) and  $H_{\text{CaO}}$  is the heat of adsorption of water on the dried  $\text{Ca}(\text{OH})_2$ . The data indicate that the heat of adsorption is considerably larger for the pastes than for the reactants, and that it becomes slightly larger as the C/S ratio increases. Older samples show less heat of adsorption of water. These phenomena may

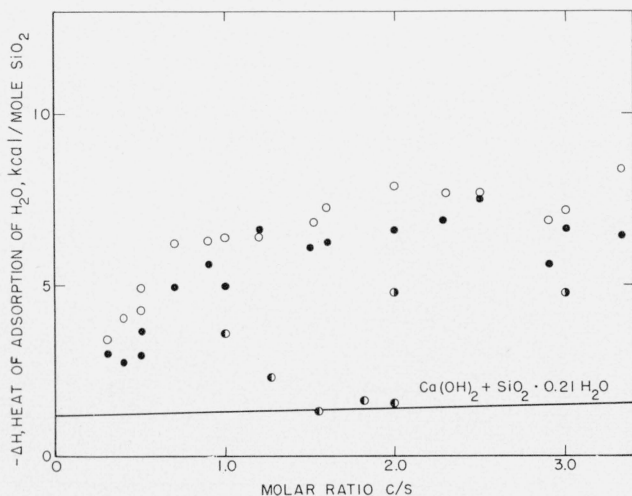


FIGURE 4.—Heat of adsorption of water on hydrated pastes.

○, 1-year, Newman; ●, 2½-year, Newman; ◐, Brunauer, Hayes, and Hass [8]; ◑, Cirilli [11, 12, 13].

be caused by differences in surface area of the materials. Brunauer et al. [8] have calculated the heat of adsorption of water on hydrated di- and tri-calcium silicate from their data combined with that of Verbeck and Foster [26] and found values corresponding to 4.8 kcal/mole of  $\text{SiO}_2$ . Their values, about 2 kcal/mole smaller than those found in the present work, are plotted in figure 4. Five values calculated from Cirilli's data are also shown.

### 3.5. Differential Thermal Analysis

Differential thermal analyses (DTA) were obtained for each sample at each age of test. Partially dried samples were tested. Figures 5, 6, and 7 show some of the curves of particular interest. Curves obtained at 16 weeks are shown in figures 5 and 6. Figure 7

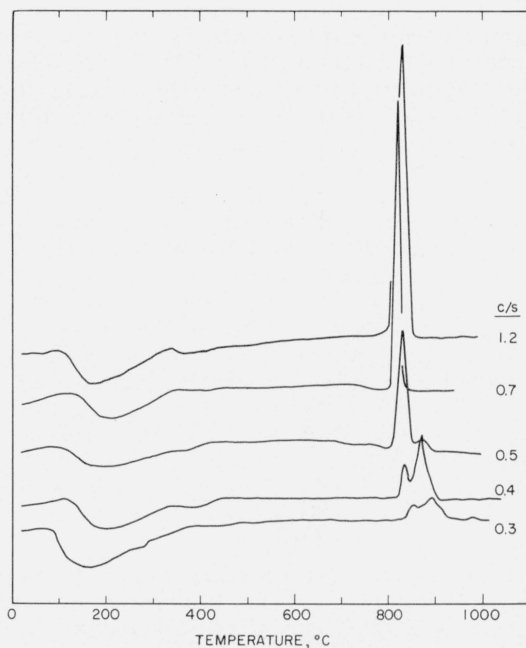


FIGURE 5.—Differential-thermal-analysis curves of pastes at 16 weeks.

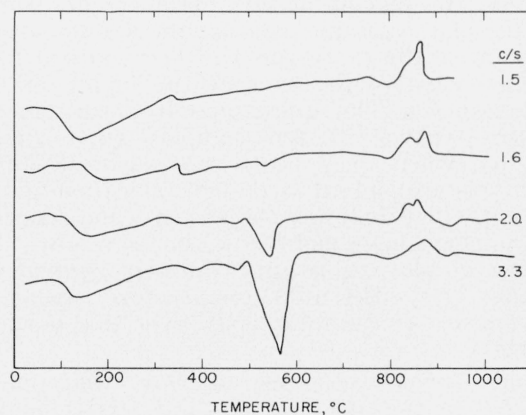


FIGURE 6.—Differential-thermal-analysis curves of pastes at 16 weeks.



shows the curves obtained at six ages of test for the sample with a C/S ratio of 1.5. All the features observed for any of the samples are shown on one or another of these curves. The curves all show a broad endotherm in the range 80° to 350° C, which is attributed in part to the loss of adsorbed and free water and which resembles that found for silica gel. Two other endotherms found in the range 350° to 500° C were assumed to be associated with the loss of chemically bound water from the hydrated calcium silicates formed in the pastes.

The presence of calcium hydroxide is clearly shown in the curves in figure 6, representing samples with C/S ratios of 1.6 or more at the age of 16 weeks. The endotherm representing its decomposition in the DTA apparatus occurs between 480° and 600° C with individual peak temperatures of 525° to 570° C in the various samples. The increased amount of calcium hydroxide with increased C/S ratio is clearly indicated by the relative sizes of the endotherms. The continued reaction of  $\text{Ca}(\text{OH})_2$  with silica gel, or with hydrated calcium silicate already formed with a C/S ratio less than 1.5, is clearly shown by the curves of figure 7, where the curves for a sample of that ratio are plotted for the different ages tested. The large amount of  $\text{Ca}(\text{OH})_2$  present at 1 day is reduced by continued reaction, as indicated by the reduced size of the endotherm with increased age, until at 16 weeks no  $\text{Ca}(\text{OH})_2$  was found by DTA. Curves not presented showed no  $\text{Ca}(\text{OH})_2$  at 1 day for samples having C/S ratios of 0.9 or less. DTA curves of all samples with C/S ratios greater than 1.5 showed the presence of  $\text{Ca}(\text{OH})_2$  at all ages tested. It is concluded from this part of the DTA curves that the calcium hydroxide reacts very rapidly with the silica gel up to a C/S ratio of about 1, and that little further reaction occurs, within the time limit of these tests, after a silicate with the C/S ratio of 1.5 has been formed.

Two exotherms representing reactions between  $\text{CaO}$  and  $\text{SiO}_2$  in the DTA apparatus were found, one at about 830° C and one at about 900° C. The exact temperatures at which they are located on the DTA curves are dependent on many variables, including the degree of packing and the size of the samples, the placing of the thermocouples, and the fraction of the sample entering the reactions, so for convenience the exotherms will be identified merely by their relative positions at the higher or lower temperature. (The approximately linear time-temperature curves of the samples were violently distorted when these exotherms occurred, but the exotherms are plotted as though each time-temperature curve had followed the straight line connecting its branches above and below the exotherms. This method of plotting is approximately equivalent to plotting the differential temperature against the temperature of the inert body over this portion of the DTA curve.)

These two exotherms indicate that changes occurred in the pastes after the  $\text{Ca}(\text{OH})_2$  had disappeared. For example, from the curves in figure 7, the exotherm at the higher temperature was the

smaller at 1 day but grew, somewhat at the expense of the other, as the age of the sample increased. The lower exotherms, however, never completely disappeared from the curve for the sample with a C/S ratio of 1.5. Similar behavior occurred at higher ratios, although the intensity of the upper exotherm was less than at 1.5. At lower C/S ratios except for the sample with a ratio of 1.2, there was practically no change of the two exotherms with age of the pastes. There was, however, a change with change in composition. As the C/S ratio increased from 0.3 to 0.7 the lower exotherm increased at the expense of the upper until the latter disappeared. At ratios of 0.7 to 1.0 only the lower exotherm was found, but at higher ratios both were again present. Up to 4 weeks the sample with a C/S ratio of 1.2 behaved like that with the 1.5 ratio, but at later ages only the lower exotherm was present.

The behavior of the exotherms indicates a change in the nature of the reacted paste between C/S ratios of 1.2 and 1.5. It must be emphasized that the exotherms represent reactions occurring in the furnace after the hydrated compounds have been destroyed, and they can not at present be related directly to the nature of the paste itself. X-ray patterns were made on samples obtained by interrupting DTA's at temperatures below, between, and above the two exotherms, but the reactions causing the exotherms were not identified. Lines of  $\text{CaO}$ , of  $\beta$  and  $\gamma\text{C}_2\text{S}$ , and  $\alpha$  and  $\beta$  CS were found in all the patterns. Kalousek [27] found similar exotherms at somewhat different temperatures for mixtures of  $\text{CaO}$  and  $\text{SiO}_2$  that had undergone hydrothermal treatment, and also for a product of the composition

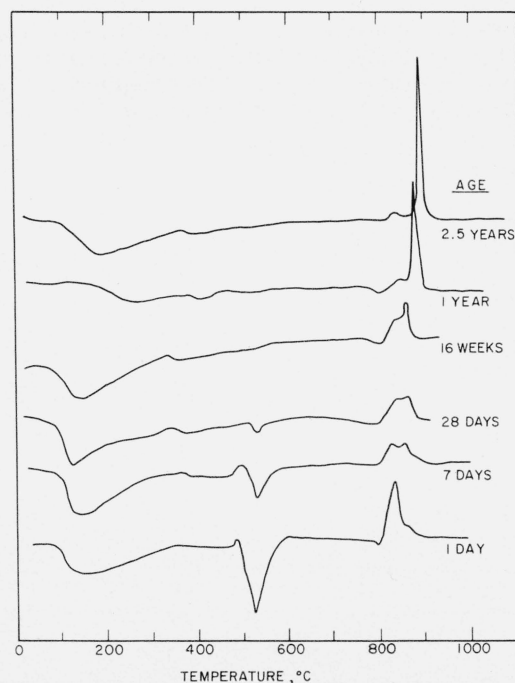


FIGURE 7.—Differential-thermal-analysis curves of pastes with C/S ratio of 1.5.

$C_5S_4H_n$  prepared at room temperature. Differences in apparatus and techniques could easily account for differences in his observed temperatures and those found here.

### 3.6. Nonevaporable Water

The nonevaporable water remaining in the dried pastes must be held in 1 of 3 ways. A portion is chemically bound in  $Ca(OH)_2$  in samples containing that material in excess either free or adsorbed. A portion is retained by the silica gel remaining in samples having a proportion of unreacted silica. The remainder of the water is retained in the calcium silicate, and a study of the data in table 1 should indicate the amount of water so held in these pastes.

Bernal [28] and Taylor [29] have given formulas corresponding to  $3CaO \cdot 2SiO_2 \cdot 3H_2O$  and  $3CaO \cdot 2SiO_2 \cdot 2H_2O$ , respectively, for the composition of one of the hydrated calcium silicates formed at room temperatures. Accordingly, computations were made from the data in table 1 to see to which, if either, of these compositions the hydrated silicate formed in the pastes corresponded. The amounts of  $SiO_2$  and  $CaO$  in the dried samples were calculated from the original C/S ratios and the losses on ignition. The water in each paste was taken as the difference between the ignition loss and the  $CO_2$  content. The total  $CaO$  was reduced by the amount assumed combined with the  $CO_2$  to form  $CaCO_3$ . It had been found that vacuum drying at room temperature would not reduce the water content of the silica gel below an H/S ratio of 0.21, and it was assumed that this amount of water was retained by any unreacted silica in the pastes. It was assumed that in pastes of C/S ratios less than 1.00 the constituents would be  $SiO_2$ ,  $0.21H_2O$  and  $CSH_n$ , and that in pastes of C/S ratios larger than 1.5 the constituents would be  $Ca(OH)_2$  and  $C_{1.5}SH_n$ . The values of  $n$  were calculated on these assumptions from the  $CaO$ ,  $SiO_2$ , and  $H_2O$  contents of the dried pastes. For the two samples with C/S ratios between 1.0 and 1.5, the values of  $n$  were cal-

culated on the assumption that  $C_mSH_n$  was formed, where  $m$  is the corrected C/S ratio of the paste.

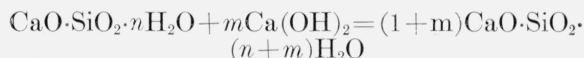
The results of these calculations are shown in figure 8, where the values of  $n$  are plotted against the corrected C/S ratios. The value of  $n$  is less than the C/S ratio at all values of C/S greater than 0.7, and is approximately 1 at C/S ratios greater than 1.5. The hydrated silicate formed in many of these pastes, therefore, appears to correspond in composition to Taylor's formula,  $3CaO \cdot 2SiO_2 \cdot 2H_2O$ .

### 4. Summary

The heat of reaction of calcium hydroxide in pastes with silica gel and water was measured by a heat-of-solution method. It was found that the heat of the reaction



is about 10.3 kcal, of which about 5 kcal is the heat of wetting of the reaction product. The heat of the reaction



is about 1.6 kcal per mole of added  $Ca(OH)_2$ .

Calcium hydroxide reacts with silica gel and water in pastes at room temperature to form hydrated calcium silicate with a C/S ratio as high as 1.5. Above that ratio the  $Ca(OH)_2$  is less firmly bound so that its presence is revealed by differential thermal analysis, although the heat of reaction per mole of silica continues to increase. Continued changes in the paste with time and with C/S ratio are indicated by changes in the behavior of the heated pastes in the DTA furnace at temperatures above  $800^\circ C$ .

Drying experiments indicated that the nonevaporable water remaining in the pastes was less than that equivalent to the  $CaO$  on a 1:1 molar basis. Above a C/S ratio of 1.5 the compositions of the dried pastes corresponded to the formula  $[3CaO \cdot 2SiO_2 \cdot 2H_2O]_x [Ca(OH)_2]_z$ .

### 5. References

- [1] H. Woods, H. H. Steinour, and H. R. Starke, *Ind. Eng. Chem.* **24**, 1207 (1932).
- [2] Federal Specification for cements, hydraulic, SS-C-158c.
- [3] ASTM Designation C186-55.
- [4] R. W. Carlson, *Proc. Am. Soc. Testing Materials* **34**, 322 (1934).
- [5] R. W. Carlson and L. R. Forbrich, *Ind. Eng. Chem., Anal. Ed.* **10**, 382 (1938).
- [6] W. Lerch, *Proc. Am. Soc. Testing Materials* **46**, 1252 (1946).
- [7] W. Lerch and R. H. Bogue, *BS J. Research* **12**, 645 (1934) RP684.
- [8] S. Brunauer, J. C. Hayes, and W. E. Hass, *J. Phys. Chem.* **58**, 279 (1954).
- [9] C. Brisi, *Ricerca sci.* **24**, 1436 (1954).
- [10] T. Thorvaldson, W. G. Brown, and C. R. Peaker, *J. Am. Chem. Soc.* **52**, 3927 (1930).
- [11] V. Cirilli, *Ricerca sci.* **10**, 459 (1939).
- [12] V. Cirilli, *Ann. chim. appl.* **28**, 151 (1938).
- [13] V. Cirilli, *Ann. chim. appl.* **28**, 239 (1938).

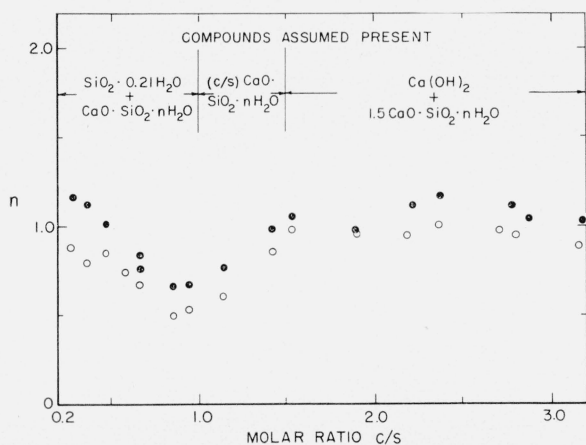


FIGURE 8.—Nonevaporable water content of hydrated pastes of calcium hydroxide and silica gel.

○, 1-year; ●, 1½-year.

- [14] International Critical Tables, National Research Council **3**, 58 (McGraw-Hill Book Co., Inc., New York, N. Y., 1933).
- [15] E. S. Newman and L. S. Wells, J. Research NBS **20**, 825 (1938) RP1107.
- [16] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Selected values of chemical thermodynamic properties, NBS Circ. 500 (U. S. Government Printing Office, Washington 25, D. C., 1952).
- [17] S. Brunauer, D. L. Kanro, and C. H. Weise, J. Phys. Chem. **60**, 771 (1956).
- [18] E. S. Newman and L. S. Wells, J. Research NBS **36**, 137 (1946) RP1696.
- [19] L. E. Copeland and J. C. Hayes, ASTM Bul. 194, p. 70 (Dec. 1953).
- [20] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, Applied inorganic analysis, 2d ed. (J. Wiley & Sons, Inc., New York, N. Y., 1953).
- [21] W. A. Roth and P. Chall, Z. Elektrochem. **34**, 185 (1928).
- [22] O. Mulert, Z. anorg. Chem. **75**, 198 (1912).
- [23] W. M. Shaw and W. H. MacIntire, Soil Sci. **29**, 429 (1930).
- [24] A. Tourky, Chemistry & Industry **1942**, 254.
- [25] S. A. Greenberg (private communication).
- [26] G. J. Verbeck and C. W. Foster, Proc. Am. Soc. Testing Materials **50**, 1235 (1950).
- [27] G. L. Kalousek, Proc. Third International Symposium, Chemistry of Cement, London, 1952, p. 299 (Cement and Concrete Assoc., 52 Grosvenor Gardens, London, SW1, 1954).
- [28] J. D. Bernal, *ibid.*, p. 233.
- [29] H. F. W. Taylor, J. Chem. Soc. **1953**, 163.

WASHINGTON, February 15, 1957.